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㉓ Zeolites.

㉔ A synthetic zeolite material, designated zeolite Nu-10, having a molar composition expressed by the following formula:

0.5 to 1.5 R₂O : Y₂O₃ : O to 4000 H₂O wherein R is a monovalent cation or 1/n of a cation of valency n, X is silicon and/or germanium, Y is one or more of aluminium, iron, chrome, vanadium, molybdenum, arsenic, antimony, manganese, gallium or boron, and H₂O is water of hydration additional to water notionally present when R is H, and having a defined X-ray pattern.

Zeolite Nu-10 is a useful catalyst for toluene methylation and the like.

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Zeolites

The present invention relates to a novel zeolite material hereinafter referred to as zeolite Nu-10, to a method of making it and to processes using it as a catalyst.

According to the present invention, we provide a
5 synthetic zeolite material, designated zeolite Nu-10, having a molar composition expressed by the following formula:
0.5 to 1.5 R_2O : Y_2O_3 : at least 20 XO_2 : 0 to 4000 H_2O
wherein R is a monovalent cation or 1/n of a cation of
valency n, X is silicon and/or germanium, Y is one or
10 more of aluminium, iron, chromium, vanadium, molybdenum,
arsenic, antimony, manganese, gallium or boron, and H_2O
is water of hydration additional to water notionally
present when R is H, and having an X-ray pattern substan-
tially as set out in Table 1 (as determined by standard
15 technique using copper K α radiation).

Zeolite Nu-10 is characterised in part by its
interplanar spacings as shown in Table 1. However, to
characterise a zeolite fully, X-ray data alone is
inadequate, and sorption and catalytic properties must
20 also be taken into account. A further feature of

zeolite Nu-10, its unique infra red spectra also helps in its characterisation.

TABLE I
X-Ray Data of Zeolite Nu-10

| d(A) | I | |
|--------------|-----|----------------|
| 10.95 ± 0.25 | m→s | |
| 8.80 ± 0.14 | w→m | |
| 6.99 ± 0.14 | w→m | |
| 5.41 ± 0.10 | w | |
| 4.57 ± 0.09 | w | |
| 4.38 ± 0.08 | vs | vs = 60 to 100 |
| 3.69 ± 0.07 | vs | s = 40 to 60 |
| 3.63 ± 0.07 | vs | m = 20 to 40 |
| 3.48 ± 0.06 | m→s | w = 0 to 20 |
| 3.36 ± 0.06 | w | |
| 3.31 ± 0.05 | w | |
| 2.78 ± 0.05 | w | |
| 2.53 ± 0.04 | m | |
| 2.44 ± 0.04 | w | |
| 2.37 ± 0.03 | w | |
| 1.88 ± 0.02 | w | |

Within the above definition, particular mention may be made of materials having a molar composition expressed by the formula:

0.5 to 1.5R₂O : Y₂O₃ : at least 60XO₂ : 0 to 200 H₂O

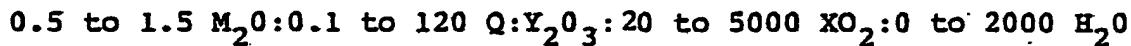
The XO₂/Y₂O₃ ratio in Nu-10 is typically in the range 20 to 5000. The sodium/organo forms of Nu-10 appear to be most readily formed when this ratio is in the range 80 to 120. On the other hand, with potassium or rubidium as inorganic cation, Nu-10 is most readily formed with a XO₂/Y₂O₃ ratio in the range 40 to 1000.

30

2. SURFACE REACTED A. COMPOUND WITH REACTED AND ONLY ONE

This definition includes both freshly prepared Nu-10 ("freshly prepared" means the product of synthesis, and washing, with optional drying, as hereinafter described) and also forms of it resulting from dehydration, 5 and/or calcination, and/or ion exchange. In freshly prepared Nu-10, R may include an alkali metal cation, especially sodium, potassium, rubidium or caesium. Ammonium and hydrogen may also be present. Usually, or when prepared from nitrogen compounds, Nu-10 includes 10 nitrogen-containing organic cations or bases as described below or cationic degradation products thereof, or precursors thereof. These nitrogen containing cations or bases are hereinafter referred to as Q.

The freshly prepared Nu-10 may also contain 15 nitrogen-containing compounds well in excess of the 1.5 moles set out in the aforesaid definition of the composition of Nu-10 typically in the range 0.1 to 120 moles per mole of Y_2O_3 . Since Nu-10 is a zeolite, the nitrogen containing base must be physically trapped within the crystal lattice. 20 It can be removed by thermal treatment and/or oxidative degradation or by displacement by suitable small molecules. This physically trapped basic material does not constitute part of the composition for the purposes of the definition. Thus Nu-10 as made typically has the following molar composition: 25



wherein M is an alkali metal and/or ammonium and can include hydrogen.

30 Among the ion-exchanged forms of zeolite Nu-10 the ammonium (NH_4^+) is of importance since it can be readily converted to the hydrogen form by calcination. The hydrogen form can also be prepared directly by exchange with an acid. The hydrogen-form and forms containing metals introduced by ion exchange are described further below. 35

The sorption results given in Table 2 were obtained on the hydrogen Nu-10 of Example 12 which had been calcined at only 450°C, and still contained carbonaceous residues (0.9% carbon by weight). When this material was further calcined for 17 hours at 550°C in moist air the carbon reduced to 0.2%^w. While the equilibrium sorption capacities were not significantly affected and were substantiated as in Table 2, the rates of sorption, except for m-xylene, were very much higher. Thus 90% equilibrium was achieved within 10 minutes and there was no significant increase in sorption of n-hexane, pyridine or p-xylene after 2 hours. On the other hand, in the HNu-10 calcined at 550°C, the m-xylene still only gave surface coverage and failed to enter the zeolite lattice.

15 These results and the results given in Table 2 suggest that zeolite Nu-10 has 10 ring ports which are a tight fit for pyridine and p-xylene at 25°C. Both diffuse in slowly after an initial modest uptake, suggesting a substantial diffusion barrier exists at 25°C for these molecules i.e. at about 5.85A. The sorption of m-xylene corresponds only to surface coverage on the zeolite Nu-10 powder. The slow uptake of n-hexane shows the channels in Nu-10 present length barriers to molecules as well as imposing restraints due to cross sectional areas. Thus
20
25 Nu-10 can be expected to show unique sorptive and catalytic properties not hitherto seen in highly siliceous zeolites. Zeolite Nu-10 should prove useful in separating aromatic compounds especially isomers e.g. xylenes and ethylbenzene, and in separating molecules not only on cross sectional area differences, but also on length differences. It is likely that substantial changes in separation processes and in shape-selective catalytic processes can be achieved by simply changing the temperature of operation and thus
30 modifying the effects of energy barriers to diffusion.

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TABLE 2 - SORPTION ON HYDROGEN Nu-10 (FROM EXAMPLE 12) AT 25°C

| Sorbate | Water | n-hexane | pyridine | p-xylene | m-xylene |
|-------------------------------|-------|----------|----------|----------|----------|
| Relative pressure P/P_0 | 0.3 | 0.33 | 0.3 | 0.5 | 0.5 |
| Kinetic diameter σ_A^* | 2.7 | 4.3 | 5.8 | 5.85 | 6.0 |
| Sorption % w/w | | | | | |
| 10 min | 3.8 | 1.8 | 2.4 | 1.7 | 0.5 |
| 1 hour | 4.0 | 2.2 | 2.6 | 1.9 | |
| 2 hour | 4.0 | 2.4 | 2.7 | 2.0 | |
| 24 hour | | 4.5 | 5.8 | 3.0 | |
| 68 hour | 4.3 | 4.8 | 6.9 | 6.3 | 0.8 |

* Lennard Jones kinetic diameter (D W Breck, "Zeolite Molecular Sieves" Wiley Interscience (1974), p 636).

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TABLE 3 - VOIDAGE AVAILABLE IN HNU-10 AT 25°C

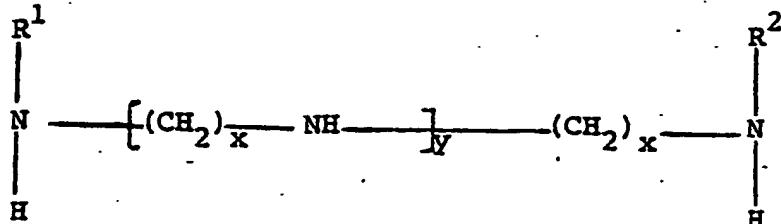
| Sorbate | Kinetic diameter Å | wt sorbed g/100g | Apparent voidage filled at equilibrium cc/100g |
|----------|-----------------------|---------------------|---|
| water | 2.7 | 4.3 | 4.3 |
| n-hexane | 4.3 | 4.8 | 7.2 |
| pyridine | 5.8 | 6.9 | 7.1 |
| p-xylene | 5.85 | 6.3 | 7.2 |
| m-xylene | 6.0 | 0.8 | 0.9 |

Table 3 gives comparative data on apparent voidage filled by different sorbates assuming that all sorbates are adsorbed as liquids, with typical liquid densities at 25°C.

Zeolite Nu-10 is further characterised by its infra-red spectrum (shown in the attached drawing). In common with other zeolites, zeolite Nu-10 has two main IR absorption regions, viz. the stretch ν of the Si-O situated near to 1100 cm^{-1} and the deformation δ of the Si-O situated near to 500 cm^{-1} . Referring to the absorptions near to 1100 cm^{-1} , zeolite Nu-10 has three distinct absorptions at 1209 cm^{-1} medium, 1117 cm^{-1} strong and 1081 cm^{-1} strong. By comparison, the absorptions near to 1100 cm^{-1} for ZSM-5 are 1228 cm^{-1} (medium) and 1095 cm^{-1} (strong). Thus there is a significant difference both in position and number of absorptions of zeolite Nu-10 as compared with the absorptions of ZSM-5.

The deformations δ near to 500 cm^{-1} of Nu-10 again shows three characteristic, clearly defined absorptions at 637 cm^{-1} (weak), 547 cm^{-1} (weak) and 463 cm^{-1} (medium strong). By comparison, ZSM-5 has a doublet absorption at 545 cm^{-1} (medium) and 455 cm^{-1} (medium). The number of absorptions, their positions and relative intensities found in the infrared spectrum of zeolite Nu-10 are sufficient to identify Nu-10 and to distinguish it from ZSM-5.

Zeolite Nu-10 may be prepared by reacting an aqueous mixture containing at least one oxide XO_2 , at least one oxide Y_2O_3 and at least one polyalkylene poly-amine having the formula:



where x is an integer from 2 to 6 and y is an integer from 0 to 10, provided that when y is 0, x is 2 to 5, an amine degradation product thereof, or a precursor thereof. In the polyamine, each of R¹ and R², independently, represents hydrogen or a C₁-C₆ alkyl group.

5 The reaction mixture preferably has the following molar ratios:

XO₂/Y₂O₃ = 25 to 5000, preferably 40 to 1000, most preferred 80 to 500

10 M¹OH/XO₂ = 10⁻⁸ to 1.0, preferably 10⁻⁶ to 0.25, most preferred 10⁻⁴ to 0.15

H₂O/XO₂ = 10 to 200, preferably 15 to 60, most preferred 30 to 50

15 Q/XO₂ = 0.05 to 4, preferably 0.1 to 1.0, most preferred 0.2 to 0.5

M²Z/XO₂ = 0 to 4.0, preferably 0 to 1.0, most preferred 0 to 0.6.

Zeolite Nu-10 can be prepared in the temperature range 20 50 to 250°C. The preferred range is 90 to 180°C and crystallization is carried out until substantially pure crystalline Nu-10 is obtained. Agitated reactions are preferred.

X is silicon or germanium, Y is aluminium, iron, 25 chromium, vanadium, molybdenum, arsenic, antimony, manganese, gallium or boron, M¹ is an alkali metal or ammonium or hydrogen, M² is an alkali metal or ammonium or hydrogen and can be the same as M¹ and Q is the aforesaid polyalkylene polyamine, amine degradation product 30 thereof or a precursor thereof, or a related compound. Z is a strong acid radical present as a salt of M² and may be added as a free acid to reduce the free M¹OH level to a desired value.

35 M²Z addition, while not essential, can accelerate crystallization of zeolite Nu-10, and can also affect

the size of crystals obtained. It should be noted that addition of M^2Z can promote the formation of α -quartz and α -cristobalite, this can usually be avoided by reducing reaction times and/or temperature to minimise the chances of overrun. If M^2Z remains intercalated within the zeolite Nu-10 framework, then it can have substantial effects on the sorption and catalytic properties. M^1 and/or Q can be present as hydroxides or salts of inorganic or organic acids provided the M^1OH/XO_2 requirement is fulfilled.

The preferred polyalkylene polyamines are triethylene tetramine and tetraethylene pentamine.

The preferred alkali metal M^1 is sodium and/or potassium M^2 is preferably the same as M^1 or is hydrogen. The preferred oxide XO_2 is silica (SiO_2) and the preferred oxide Y_2O_3 is alumina (Al_2O_3).

The silica source can be any of those commonly considered for use in synthesising zeolites, for example powdered solid silica, silicic acid, colloidal silica or dissolved silica. Among the powdered silicas usable are precipitated silicas, especially those made by precipitation from an alkali metal silicate solution, such as the type known as "KS 300" made by AKZO, and similar products aerosil silicas, fume silicas and silica gels suitably in grades for use in reinforcing pigments for rubber or silicone rubber. Colloidal silicas of various particle sizes may be used, for example 10-15 or 40-50 microns, as sold under the Registered Trade Marks "LUDOX" "NALCOAG" and "SYTON". The usable dissolved silicas include commercially available waterglass silicates containing 0.5 to 0.6, especially 2.0 to 4.0 mols of SiO_2 per mol of alkali metal oxide, "active" alkali metal silicates as defined in UK Patent 1193254, and silicates made by dissolving silica in alkali metal hydroxide or quaternary ammonium hydroxide or a mixture thereof.

The alumina source is most conveniently sodium aluminate, but can be or can include aluminium, an aluminium salt for example the chloride, nitrate or sulphate, an aluminium alkoxide or alumina itself, which 5 should preferably be in a hydrated or hydratable form such as colloidal alumina, pseudoboehmite, boehmite, gamma alumina or the alpha or beta trihydrate.

The reaction mixture is reacted usually under autogenous pressure, optionally with added gas, e.g. 10 nitrogen at a temperature between 50 and 250°C until crystals of Nu-10 form, which can be from 1 hour to many months depending on the reactant composition and the operating temperature. Agitation is optional, but is preferable since it reduces the reaction time. If 15 agitation is inadequate, or the reaction is carried out under quiescent conditions, then there is a distinct probability of producing zeolite Nu-10 contaminated by ZSM5 family zeolites, such as zeolite Nu-4 of our copending UK Patent Application No. 8115407.

20 In order to prepare the best possible adsorbents and catalysts from zeolite Nu-10, it is essential that the levels of ZSM5 family zeolites are negligible, because ZSM5 family zeolites give rise to undesirable side effects as a result of their inferior shape-size- 25 selectivity-performance as compared with the unique and highly desirable properties of zeolite Nu-10 for certain applications, for example including but not limited to the separation of aromatic isomers, toluene methylation, and dehydration of alcohols.

30 The synthesis of zeolite Nu-10 in substantially pure form can be guaranteed by strict adherence to the narrow range conditions. For reaction mixture compositions in the wider ranges, substantially pure Nu-10 can still be obtained, especially where the more important narrow 35 range criteria such as XO_2/Y_2O_3 , $M^{10}H/XO_2$ and temperature/time are met. Time/temperature becomes more critical in

the wider range and overrun to α -quartz and α -cristobalite becomes more likely. This tendency can be reduced by using potassium or rubidium as the alkali cations. To those skilled in the art it will be apparent, from 5 examples given, that even in the wider reaction mixture ranges, many combinations will still give Nu-10 as the major component, and that with care it will be possible to prepare pure Nu-10.

If mixtures of zeolite Nu-10 and ZSM5 family 10 zeolites are desired then this can be achieved by deliberately operating at XO_2/Y_2O_3 ratios below 70 and $NaOH/XO_2$ greater than 0.06.

At the end of the reaction, the solid phase is collected on a filter and washed and is then ready for 15 further steps such as drying, dehydration and ion-exchange.

If the product of the reaction contains alkali metal ions, these have to be at least partly removed in order to prepare more acid forms of Nu-10 and this can 20 be done by ion exchange with an acid, especially a strong mineral acid such as hydrochloric acid or by way of the ammonium compound, made by ion exchange with a solution of an ammonium salt such as ammonium chloride. Such ion exchange can be carried out by slurring once or 25 several times with the solution.

In general, the cation(s) of zeolite Nu-10 can be replaced by any cation(s) of metals, and particularly those in Groups IA, IB, IIA, IIB, III (including rare 26 earths) VIII (including noble metals) and by lead, tin and bismuth. (The Periodic Table is as in "Abridgements of Specifications" published by the UK Patent Office). Exchange is carried out using any water soluable salts containing the appropriate cation.

30 In order to prepare a catalyst, zeolite Nu-10 may be used in association with an inorganic matrix, or

with other materials which can be either inert or catalytically active. The matrix may be present simply as a binding agent to hold the small zeolite particles (0.005 to 10 microns) together, or it may be added as a 5 diluent to control the amount of conversion in a process which may otherwise proceed at too high a rate, leading to catalyst fouling as a result of excessive coke formation. Typical inorganic diluents include catalyst support materials such as alumina, silica, kaolinic clays, 10 bentonites, montmorillonites, sepiolite, attapulgite, Fullers earth, synthetic porous materials such as SiO_2 - Al_2O_3 , SiO_2 - ZrO_2 , SiO_2 - ThO_2 , SiO_2 - BeO , SiO_2 - TiO_2 or any combination of these oxides. An effective way of mixing zeolite Nu-10 with such diluents is to mix appropriate 15 aqueous slurries in a mixing nozzle and then to spray dry the slurry. Other ways of mixing can be used.

If zeolite Nu-10 in any cationic form or as a catalytic composite is exchanged or impregnated with hydrogenation/dehydrogenation components, such as Ni, 20 Co, Pt, Pd, Re, Rh, hydrocracking and reforming catalysts can be made, especially if the Na_2O content is less than 0.1% w/w.

A wide range of hydrocarbon conversion catalysts can be prepared from zeolite Nu-10 by ion exchange or 25 impregnation with cations, or oxides, selected from the following, Cu, Ag, Mg, Ca, Sr, Zn, Cd, B, Al, Sn, Pb, V, P, Sb, Cr, Mo, W, Mn, Re, Fe, Co, Ni and noble metals.

Usually, the Nu-10 catalyst will be in acid form thus stoichiometry is maintained by H^+ or H_3O^+ as an 30 additional balancing cation, or as sole cation. Such catalysts may find application in the following processes: catalytic cracking, hydrodesulphurization, hydrodenitration, catalytic dewaxing, alkylation of alkanes or aromatics, dealkylation, disproportionation, isomerisation 35 of alkanes and alkyl benzenes, dehydration reactions, oxidation and polymerisation.

Particular mention may be made of an alkylation process which comprises contacting an alkyl-benzene or a mixture of alkybenzenes and an alkylating agent under alkylation conditions in the vapour or liquid phase with a catalyst comprising zeolite Nu-10.

The alkylbenzene starting materials include toluene, ortho-, meta- and para- xlenes, ethylbenzene, trimethylbenzene, tetramethylbenzene, and the like, or mixtures thereof. The alkylation process is especially applicable to the use of toluene as the starting material.

Suitable alkylating agents include alkanols, alkyl halides, alkyl ethers, alkyl sulphides and olefins.

Preferred methylating agents include methanol, methyl chloride, methyl bromide, methyl carbonate, dimethyl ether and dimethyl sulphide. The use of methanol as the methylating agent is especially preferred.

The molar ratio of the alkylating agent to the alkylbenzene is generally between about 0.005 and about 5, for example between about 0.1 and about 3.

An especially preferred alkylation process comprises the methylation of toluene using methanol as the methylating agent to give a product comprising the xylene isomers, and in particular to a process for the selective production of para-xylene from toluene and methanol, the said para-xylene being obtained in excess of its normal equilibrium concentration (which is about 23-24%) of the xylene isomers with limited production of higher methylbenzenes.

The alkylation process, e.g. methylation, is suitably carried out at a temperature in the range of about 250 to about 750°C, preferably about 350°C, to about 600°C, at a pressure between 1 atmosphere abs and about 60 atmosphere abs and at a WHSV of 1 to about 1500.

Mention may also be made of a process for the

production of hydrocarbons which comprises contacting a lower monohydric alcohol or an ether derived therefrom under conversion conditions with a catalyst comprising zeolite Nu-10.

5 Lower monohydric alcohols which may be used in this process particularly include saturated monohydric alcohols containing up to four carbon atoms in the molecule. Ethers which may be used include the symmetrical and unsymmetrical ethers derived from the aforesaid
10 alcohols by dehydration. If desired, mixtures of alcohols and/or ethers may be used. It is particularly preferred to use methanol and/or dimethyl ether as the starting material(s).

15 This process is suitably carried out at a temperature in the range 250-700°C and preferably in the range 350-500°C. The pressure is suitably in the range 0.2-50 atm abs, preferably 0.5 to 20 atm abs. The weight hourly space velocity (WHSV) is typically in the range of about 0.5 to 50.

20 The products of the reaction, which include lower olefins, especially C₂ to C₇ olefins, particularly propylene and butylenes, and smaller amounts of some aromatic hydrocarbons such as benzene, toluene and xylenes, may be recovered and separated using conventional
25 methods.

The catalyst may be in the form of a fixed bed, fixed fluid bed or it may be of the transport type.

The catalyst as used maintains its activity for a substantial period, but can be regenerated by heating.

30 For example, when the catalyst is used in the form of a fluidised bed, the catalyst may be continuously withdrawn, passed through a regeneration zone and returned to the reaction.

35 Zeolite Nu-10 may also find applications in pollution control by its ability to remove organic con-

taminants from aqueous effluents.

The invention is illustrated by the following Examples.

Example 1

5 Preparation of sodium tetraethylene pentamine (TEPA) Nu-10 and sodium Nu-10.

The synthesis mixture had the following molar composition:

2.34 Na₂O, 27 TEPA, Al₂O₃, 96.6 SiO₂, 3878 H₂O, 54.8 NaCl

10 38g TEPA were dispersed in 142g colloidal silica (Syton X-30). Next, 1.6g sodium aluminate (1.25 Na₂O, Al₂O₃, 3H₂O) dissolved in 10g water were stirred into the silica suspension followed by 23g sodium chloride dissolved in 388g water. The resulting gel was mixed 15 thoroughly for $\frac{1}{2}$ hour to a homogeneous texture, and was then reacted for 3 days at 180°C in a 1 litre stainless steel stirred autoclave under autogenous pressure. The stirrer speed was maintained at 500 rpm. After cooling to about 60°C, the slurry was filtered and washed with 20 2 litres of distilled water at 60°C and dried overnight at 120°C. The product was sodium TEPA Nu-10 with X-ray diffraction data as shown in Table 4.

Example 2

25 The product of Example 1 was calcined in moist air for 48 hours at 450°C and its X-ray diffraction pattern was substantially unchanged. Next, it was slurry-exchanged for 1 hour at 25°C with 4 ml of N hydrochloric acid per g of zeolite. The resulting hydrogen Nu-10 was washed with 30 10 ml of distilled water per g of zeolite, dried overnight at 120°C, and calcined in moist air for 6 hours at 450°C. Its X-ray diffraction data were still substantially as given in Table 4.

Example 3

35 This Example was the same as Example 1 except that TEPA was replaced by a molar equivalent of triethylene tetramine (TETA). The product after 3 days at 180°C was sodium TETA NU-10, as shown by x-ray data given in Table 5.

TABLE 4

| | | | | | | | | |
|----------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| da | 10.9 | 9.94 | 8.76 | 6.97 | 5.373 | 4.575 | 4.353 | 4.095 |
| 100 ¹ /10 | 40 | 11 | 6 | 11 | 9 | 10 | 100 | 26* |
| da | 3.663 | 3.619 | 3.466 | 2.988 | 2.818 | 2.522 | 2.493 | 2.439 |
| 100 ¹ /10 | 94 | 74 | 31 | 8 | 8* | 26 | 5* | 8 |

* due at least in part to α -cristobalite

TABLE 5

| | | | | | | | |
|----------------------|-------|-------|-------|-------|-------|-------|-------|
| dA | 10.9 | 6.97 | 5.373 | 4.564 | 4.353 | 4.086 | 3.678 |
| 100 ¹ /10 | 11 | 13 | 10 | 10 | 100 | 32* | 90 |
| dA | 3.619 | 3.480 | 2.818 | 2.522 | 2.495 | 2.436 | 2.362 |
| 100 ¹ /10 | .72 | .34 | .25 | .22 | .9* | 11 | 10 |

* due at least in part to α -cristobalite

Example 4

5 This example demonstrates that if high levels of TETA are employed then reaction times must be reduced or substantial contamination by α -cristobalite occurs. The Example was exactly as Example 3 but 94.9g of TETA were used instead of 27.2g which corresponds to an increase in the Q/SiO_2 ratio of from 0.28 to 0.94. The product after 2 days was Nu-10 with about 5% cristobalite as an impurity, but after 3 days the α -cristobalite level had increased to about 25%

10

Example 5

15 This example illustrates that zeolite Nu-10 can be prepared from mixtures containing very little free alkali e.g. $M^1OH/SiO_2 = 0.0099$. The molar composition of the mixture was:

18 TEPA, 0.48 Na_2O , Al_2O_3 , 96.3 SiO_2 , 3600 H_2O , 54 NaCl, 1.82 Na_2SO_4 .
18g TEPA were dispersed in 152g colloidal silica. Next 1.5g sodium aluminate (1.19 Na_2O , Al_2O_3 , 1.29 H_2O) dissolved in 10 g water were stirred in, followed by 24.3g sodium chloride and 1.4g concentrated sulphuric acid in 458 g water. The reaction was carried out as in Example 1, except that the reaction time was 3½ days. The product was an excellent sample of zeolite Nu-10.

20

Example 6

25 This Example illustrates that for some reaction mixture compositions with SiO_2/Al_2O_3 ratio greater than about 200, zeolite Nu-10 can be very heavily contaminated. The molar composition of the reaction mixture was:

30 7.36 Na_2O , 281 TETA, Al_2O_3 , 300 SiO_2 , 11293 H_2O , 166 NaCl. The mixture was reacted at $180^{\circ}C$ for 3 days with stirrer speed 500 rpm and the product contained about 60% α -quartz and approximately equal amounts of zeolite Nu-10, zeolite Nu-4 and α -cristobalite. The products after 1 and 2 days contained only amorphous materials.

35

Example 7

Sodium tetraethylene pentamine Nu-10 was prepared as follows:

Solution A

5 142 g SYTON X30 colloidal silica (Monsanto chemicals of molar composition 27 Na_2O : 2400 SiO_2 : Al_2O_3 : 19550 H_2O)
37.8 g Tetraethylenepentamine (TEPA) - "Technical" grade British Drug Houses).

Solution B

10 1.6 g Sodium Aluminate ("Technical" grade, British Drug Houses, of molar composition 1.22 Na_2O : Al_2O_3 : 1.02 H_2O)

10 g Deionised water

Solution C

15 22.5g Sodium chloride ("Analar" grade, British Drug Houses)

388g Deionised water

This reaction mixture had the following molar composition:

20 2.14 Na_2O : 84 SiO_2 : Al_2O_3 : 25 TEPA : 48 NaCl : 3421 H_2O
Solution A was introduced into a one litre 316 stainless steel autoclave, equipped with an air driven magnedrive turbine stirrer (manufactured by Autoclave Engineers).

Solution B was added with stirring at ambient temperature.

25 Solution C was then added with stirring until a homogenous gel was produced. After sealing the autoclave, the reaction mixture was maintained under autogenous pressure with stirring (approximately 1000 rpm) at 180°C for 5 days.

At the end of this time, the reaction mixture was cooled to room temperature and the product filtered and washed with deionised water (3 litres) and dried for several hours at 150°C, yield ca. 40g.

Examination of the crystals by scanning electron microscopy (SEM) showed these to be needles of uniform

width of 500 Å and lengths varying between $\frac{1}{2}$ and 1 μ .

The product exhibited an X-ray powder diffraction pattern

as shown in Table 6 and the following elemental analyses :

Carbon 2.84 wt%, Hydrogen 0.67 wt%, Nitrogen 1.65 wt%,

5 Silicon 42.9 wt%, Aluminium 0.95 wt%. The product had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 87.

TABLE 6

X-Ray data of Sodium T.E.P.A. Nu-10 Prepared as described
in Example 7

10

| | Interplanar Spacing d (Å) | Relative Intensity | |
|----|------------------------------|--------------------|------------------|
| | | 100 | I/I ₀ |
| 15 | 10.77 | | 49 |
| | 8.66 | | 19 |
| | 6.91 | | 19 |
| | 5.40 | | 13 |
| | 4.53 | | 16 |
| | 4.33 | 100 | |
| 20 | 4.07 | | 69* |
| | 3.66 | | 98* |
| | 3.62 | | 85 |
| | 3.46 | | 36 |
| | 2.51 | | 58* |
| | 2.43 | 14 | |
| 25 | 2.37 | | 9 |
| | 1.87 | | 8 |
| | 1.60 | | 8 |
| | 1.43 | | 9 |
| | | | |
| | | | |

30

* due at least in part to α -cristobalite

The hydrogen form of Nu-10 was prepared by calcining 10g of the above product in air at 450°C for 17 hours, then exchanging at ambient temperature with 0.1 molar hydrochloric acid solution (ca. 300 cm³) for several hours and finally drying at 150°C for 3 hours. This

35

hydrogen Nu-10 had the following elemental analysis. Carbon 0.44 wt%, Hydrogen 0.31 wt%, Nitrogen < 0.02 wt%, Silicon 44.4 wt%, Aluminium 0.94 wt%. $\text{SiO}_2/\text{Al}_2\text{O}_3$ was 91.

Example 8

5 The reaction was carried out as in Example 7 with the exception that 1.6g NALFLOC sodium aluminate (of molar composition 1.23 $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 2.8 \text{H}_2\text{O}$) was used at a reaction temperature of 150°C for 3½ days. The reaction mixture had the following molar composition:

10 $2.24 \text{Na}_2\text{O} : 95 \text{SiO}_2 : \text{Al}_2\text{O}_3 : \text{T E P A} : 53 \text{NaCl} :$
3852 H_2O

The product was shown by S.E.M. to be 1000 to 1500 Å diameter by 2 to 3 μ long needles and exhibited the X-ray powder diffraction of sodium T E P A Nu-10 as shown in

15 Table 7. It was calcined and exchanged as in Example 7. The respective X-ray data of the resulting sodium/hydrogen Nu-10 and the hydrogen Nu-10 are also included in Table 7.

Example 9

20 The reaction was carried out as in Example 7 with the exception that the reaction was at a temperature of 150°C for 4 days. The product was shown to be 500 to 1000 Å diameter by 1 to 2 μ long needles by S.E.M. and exhibited an X-ray powder diffraction as shown in Table 8. The product was calcined and exchanged as in Example 7.

25 Example 10

The reaction was carried out as in Example 7 with the exception that the reaction was at a temperature of 120°C for 10 days. The product exhibited an X-ray powder diffraction as shown in Table 9.

30 Example 11

The reaction was carried out as in Example 7 with the exception that 18.9g of T E P A. was used at a reaction temperature of 105°C for 40 days. The product exhibited

an X-ray powder diffraction as shown in Table 10.

Example 12

The molar composition of the synthesis mixture was
2.32 Na_2O , 90.6 TETA, Al_2O_3 , 96.3 SiO_2 , 3862 H_2O
5 94.5 g TETA were dispersed in 141.5g colloidal silica,
followed by a solution of 1.6g sodium aluminate in
396.5g water. The mixture was homogenised for 30 minutes.
and then transferred to a 1 litre stainless steel auto-
calve. The reaction was carried out as in Example 1.
10 The dried product was a very pure sample of sodium TETA
Nu-10 zeolite of molar composition:

1.08 Na_2O ; 2.7 TETA, Al_2O_3 , 90 SiO_2 , 12 H_2O
and consisted of rod shaped crystals with dimensions 1 μm
15 long by 0.1 μm thick.

X-ray diffraction data is given in Table 11.
A portion of this product was calcined in air at
450°C for 72 hours. The resulting sodium hydrogen Nu-10
had the X-ray data shown in Table 11.

20 The sample of sodium hydrogen Nu-10 was slurry
exchanged for 1 hour at 60°C with 5 ml per g of normal
hydrochloric acid. The product was filtered and washed
twice with 10 ml/g of distilled water, dried at 120°C
and finally calcined for 3 hours at 450°C in air. Its
25 molar composition was:

0.07 Na_2O , Al_2O_3 , 92.1 SiO_2
and it contained 0.9% w/w carbon and had the X-ray dif-
fraction data shown in Table 11.

30 This hydrogen Nu-10 product consisted of needles 1.0-1.5 μm
in length and 0.1 μm in thickness and there was very
substantial twinning. The crystal type was C centred
orthorhombic with a probable space group CMCM and unit

TABLE 7

| Sodium TEPA Nu-10 | | Sodium Hydrogen Nu-10 | | Hydrogen Nu-10 | |
|-------------------|-------------|-----------------------|-------------|----------------|-------------|
| d (Å) | $100 I/I_0$ | d (Å) | $100 I/I_0$ | d (Å) | $100 I/I_0$ |
| 10.64 | 36 | 10.77 | 57 | 10.64 | 61 |
| 8.58 | 17 | 8.66 | 23 | 8.58 | 19 |
| 6.91 | 17 | 6.91 | 28 | 6.86 | 24 |
| 5.37 | 12 | 5.40 | 17 | 5.37 | 18 |
| 4.55 | 17 | 4.55 | 17 | 4.53 | 19 |
| 4.35 | 98 | 4.33 | 100 | 4.33 | 99 |
| 3.64 | 100 | 3.66 | 91 | 3.64 | 100 |
| 3.60 | 74 | 3.62 | 66 | 3.59 | 67 |
| 3.45 | 40 | 3.45 | 37 | 3.44 | 41 |
| 2.51 | 24 | 2.51 | 22 | 2.51 | 23 |
| 2.43 | 10 | 2.43 | 12 | 2.43 | 12 |
| 2.35 | 7 | 2.36 | 8 | 2.35 | 9 |
| 1.87 | 7 | 1.87 | 9 | 1.86 | 8 |
| 1.59 | 5 | | | | - |

TABLE 8

X-ray data of Sodium T E P A Nu-10 Prepared
as described in Example 9

| Interplanar Spacing d (Å) | Relative Intensity | |
|------------------------------|--------------------|------------------|
| | 100 | I/I ₀ |
| 10.91 | | 48 |
| 8.75 | | 18 |
| 6.91 | | 19 |
| 5.40 | | 12 |
| 4.55 | | 16 |
| 4.35 | 100 | |
| 3.66 | | 96 |
| 3.62 | | 78 |
| 3.46 | | 39 |
| 2.51 | | 26 |
| 2.43 | | 12 |
| 2.36 | | 8 |

TABLE 9
X-Ray data of Sodium T.E.P.A. Nu-10
prepared as described in Example 10

| Interplanar Spacing d (Å) | Relative Intensity 100 I/I ₀ |
|--------------------------------|--|
| 10.77 | 44 |
| 8.66 | 16 |
| 6.96 | 17 |
| 5.40 | 14 |
| 4.57 | 14 |
| 4.35 | 94 |
| 3.66 | 100 |
| 3.62 | 79 |
| 3.48 | 38 |
| 2.51 | 14 |
| 2.43 | 11 |
| 2.36 | 10 |

TABLE 10

X-Ray data of Sodium T.E.P.A. Nu-10
prepared as described in Example 11

| Interplanar Spacing d (Å) | Relative Intensity 100 I/I ₀ | Interplanar Spacing d (Å) | Relative Intensity 100 I/I ₀ |
|--------------------------------|--|--------------------------------|--|
| 10.77 | 44 | 10.77 | 48 |
| 8.66 | 16 | 8.66 | 17 |
| 6.96 | 17 | 6.91 | 18 |
| 5.40 | 14 | 5.37 | 12 |
| 4.57 | 14 | 4.55 | 15 |
| 4.35 | 94 | 4.35 | 96 |
| 3.66 | 100 | 3.66 | 100 |
| 3.62 | 79 | 3.62 | 77 |
| 3.48 | 38 | 3.46 | 40 |
| 2.51 | 14 | 2.51 | 24 |
| 2.43 | 11 | 2.44 | 12 |
| 2.36 | 10 | 2.36 | 8 |

TABLE 11

X-ray data for zeolite Nu-10 (Example 12)

| As-made Nu-10 | | Sodium Hydrogen Nu-10 | | | Hydrogen Nu-10 | |
|---------------|----------------------------------|-----------------------|----------------------------------|-------|----------------------------------|--|
| da | 100 ^I /I ₀ | da | 100 ^I /I ₀ | da | 100 ^I /I ₀ | |
| 11.19 | 51 | 10.92 | 78 | 10.98 | 66 | |
| 8.93 | 6 | 8.76 | 14 | 8.76 | 11 | |
| 6.970 | 16 | 6.971 | 20 | 6.971 | 18 | |
| 5.471 | 9 | 5.439 | 13 | 5.422 | 12 | |
| 4.611 | 12 | 4.576 | 13 | 4.588 | 12 | |
| 4.418 | 97 | 4.375 | 100 | 4.375 | 100 | |
| 3.708 | 100 | 3.693 | 92 | 3.693 | 90 | |
| 3.655 | 75 | 3.626 | 63 | 3.626 | 65 | |
| 3.500 | 38 | 3.467 | 34 | 3.467 | 30 | |
| 3.370 | 10 | 3.347 | 8 | 3.339 | 6 | |
| 3.320 | 8 | 3.303 | 7 | 3.303 | 5 | |
| 2.536 | 20 | 2.526 | 20 | 2.529 | 22 | |
| 2.449 | 11 | 2.439 | 9 | 2.439 | 9 | |
| 2.380 | 7 | 2.374 | 6 | 2.371 | 7 | |
| - | - | 2.067 | 5 | 2.072 | 4 | |
| - | - | 2.038 | 5 | 1.907 | 3 | |
| 1.884 | 6 | 1.870 | 3 | 1.874 | 7 | |

TABLE 12

x-ray data of Potassium, sodium TEPA Nu-10 of Example 19

| | Interplanar Spacing d(Å) | Relative Intensity 100 I/I_0 |
|----|-----------------------------|-----------------------------------|
| 5 | 10.79 | 59 |
| 10 | 8.93 | 4 |
| | 8.68 | 9 |
| 15 | 7.22 | 3 |
| | 6.93 | 12 |
| 20 | 5.40 | 10 |
| | 5.32 | 7 |
| 25 | 4.543 | 7 |
| | 4.355 | 61 |
| | 3.665 | 87 |
| 30 | 3.616 | 100 |
| | 3.467 | 45 |
| 35 | 3.342 | 8 |
| | 3.215 | 2 |
| | 2.971 | 3 |
| | 2.938 | 4 |
| | 3.898 | 4 |
| | 2.777 | 4 |
| | 2.736 | 5 |
| | 2.518 | 14 |
| | 2.451 | 9 |
| | 2.435 | 12 |
| | 2.366 | 8 |
| | 2.066 | 4 |
| | 2.037 | 5 |
| | 2.001 | 4 |
| | 1.900 | 5 |
| | 1.878 | 8 |

cell a = 13.853, b = 17.434, c = 5.040.

Example 13

The molar composition of the reaction mixture was
5 3.6 Na₂O, 42.6 TETA, Al₂O₃, 150 SiO₂, 6000 H₂O, 54 NaCl
The reaction was carried out as in Example 1. The product
contained about 85% zeolite Nu-10 along with 15% α -
crytobalite.

10 Example 14
The molar composition of the reaction mixture was

1.21 Na₂O, 26 TETA, Al₂O₃, 96.3 SiO₂, 2014 H₂O, 54.8 NaCl
The reaction was carried out as in Example 1.
A sample withdrawn after 48 hours was substantially pure
zeolite Nu-10, but the product after 72 hours at 180°C
15 was zeolite Nu-10 plus about 40% α -cristobalite

Example 15
The synthesis mixture had the following molar composition.
8.4 Na₂O, 57O, Al₂O₃, 170. SiO₂, 8500 H₂O

20 51g of solid silica (Degussa Aerosil 200) were dispersed
in a mixture of 24 g ethylene diamine and 740 g water.
Next, 1g sodium aluminate(1.22 Na₂O₂, Al₂O₃, 1.9 H₂O) and 5.3g
sodium hydroxide were dissolved in 25g water. Finally, the
25 aluminate solution was stirred into the silica suspension
and then reacted for 6 days at 150°C in a stirred stainless
steel 1 litre autoclave. The product was Nu-10 having an
SiO₂/Al₂O₃ of 165.

Example 16
30 This Example illustrates that symmetrically di-substituted
ethylene diamines can be used in Nu-10 synthesis.

The synthesis mixture had the following molar composition
143 K₂O, 54O, Al₂O₃, 170 SiO₂, 8000 H₂O
48g. Aerosil 200 were dispersed in a mixture of 29.5 g
N, N¹-diethyl ethylene diamine and 702g water. Next 0.75g
35 Kaiser S.A. alumina were dissolved in 7.5g potassium
hydroxide and 16.5g water. The aluminate solution was

stirred into the silica suspension and reacted for 41 hours at 180°C in a stirred 1 litre stainless steel autoclave. The Nu-10 product had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ of 169.

By contrast, when unsymmetrical N, N-diethyl 5 ethylene diamine was used the reaction yielded a pure sample of zeolite Nu-4 of our copending application Number 8115407.

Example 17

This Example was exactly as Example 1 except that 10 20.5g ethylene diamine replaced the TEPA. The reaction was for 5 days at 150°C and the product was Nu-10.

Example 18

The synthesis mixture had the following molar composition.

1.89 Na_2O , 20.40 Al_2O_3 , 60.5 SiO_2 , 2563 H_2O , 32.0 NaCl ,

15 1.69 H_2SO_4

First, 43g of TEPA and 141g colloidal silica were mixed. Next, 2.2g sodium aluminate (1.09 Na_2O , Al_2O_3 , 2.33 H_2O) dissolved in 10g water were stirred in followed by 20g sodium chloride and 1.8g concentrated sulphuric acid in 20 380g water.

The effective OH^-/SiO_2 of this reaction was 0.007. The mix was reacted for 4 days at 180°C and the NU-10 product had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 56.

Example 19

25 The synthesis mixture had the following composition.

1.22 Na_2O , 40.8 K_2O , 120 TEPA, Al_2O_3 , 500 SiO_2 , 25,000 H_2O

46g Degussa Aerosil 200 were dispersed in 35g TEPA

and 660g water. Next, 0.3g sodium aluminate (1.22 Na_2O , Al_2O_3 , 1.2 H_2O) and 7g potassium hydroxide were dissolved in

30 31g water, and then were mixed into the silica suspension. The mixture was reacted for 5 days at 180°C in a stirred stainless steel autoclave. The product was a highly crystalline potassium, sodium TEPA Nu10 having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ = 492 and the X-ray data given in Table 12.

25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000 1005 1010 1015 1020 1025 1030 1035 1040 1045 1050 1055 1060 1065 1070 1075 1080 1085 1090 1095 1100 1105 1110 1115 1120 1125 1130 1135 1140 1145 1150 1155 1160 1165 1170 1175 1180 1185 1190 1195 1200 1205 1210 1215 1220 1225 1230 1235 1240 1245 1250 1255 1260 1265 1270 1275 1280 1285 1290 1295 1300 1305 1310 1315 1320 1325 1330 1335 1340 1345 1350 1355 1360 1365 1370 1375 1380 1385 1390 1395 1400 1405 1410 1415 1420 1425 1430 1435 1440 1445 1450 1455 1460 1465 1470 1475 1480 1485 1490 1495 1500 1505 1510 1515 1520 1525 1530 1535 1540 1545 1550 1555 1560 1565 1570 1575 1580 1585 1590 1595 1600 1605 1610 1615 1620 1625 1630 1635 1640 1645 1650 1655 1660 1665 1670 1675 1680 1685 1690 1695 1700 1705 1710 1715 1720 1725 1730 1735 1740 1745 1750 1755 1760 1765 1770 1775 1780 1785 1790 1795 1800 1805 1810 1815 1820 1825 1830 1835 1840 1845 1850 1855 1860 1865 1870 1875 1880 1885 1890 1895 1900 1905 1910 1915 1920 1925 1930 1935 1940 1945 1950 1955 1960 1965 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015 2020 2025 2030 2035 2040 2045 2050 2055 2060 2065 2070 2075 2080 2085 2090 2095 2100 2105 2110 2115 2120 2125 2130 2135 2140 2145 2150 2155 2160 2165 2170 2175 2180 2185 2190 2195 2200 2205 2210 2215 2220 2225 2230 2235 2240 2245 2250 2255 2260 2265 2270 2275 2280 2285 2290 2295 2300 2305 2310 2315 2320 2325 2330 2335 2340 2345 2350 2355 2360 2365 2370 2375 2380 2385 2390 2395 2400 2405 2410 2415 2420 2425 2430 2435 2440 2445 2450 2455 2460 2465 2470 2475 2480 2485 2490 2495 2500 2505 2510 2515 2520 2525 2530 2535 2540 2545 2550 2555 2560 2565 2570 2575 2580 2585 2590 2595 2600 2605 2610 2615 2620 2625 2630 2635 2640 2645 2650 2655 2660 2665 2670 2675 2680 2685 2690 2695 2700 2705 2710 2715 2720 2725 2730 2735 2740 2745 2750 2755 2760 2765 2770 2775 2780 2785 2790 2795 2800 2805 2810 2815 2820 2825 2830 2835 2840 2845 2850 2855 2860 2865 2870 2875 2880 2885 2890 2895 2900 2905 2910 2915 2920 2925 2930 2935 2940 2945 2950 2955 2960 2965 2970 2975 2980 2985 2990 2995 3000 3005 3010 3015 3020 3025 3030 3035 3040 3045 3050 3055 3060 3065 3070 3075 3080 3085 3090 3095 3100 3105 3110 3115 3120 3125 3130 3135 3140 3145 3150 3155 3160 3165 3170 3175 3180 3185 3190 3195 3200 3205 3210 3215 3220 3225 3230 3235 3240 3245 3250 3255 3260 3265 3270 3275 3280 3285 3290 3295 3300 3305 3310 3315 3320 3325 3330 3335 3340 3345 3350 3355 3360 3365 3370 3375 3380 3385 3390 3395 3400 3405 3410 3415 3420 3425 3430 3435 3440 3445 3450 3455 3460 3465 3470 3475 3480 3485 3490 3495 3500 3505 3510 3515 3520 3525 3530 3535 3540 3545 3550 3555 3560 3565 3570 3575 3580 3585 3590 3595 3600 3605 3610 3615 3620 3625 3630 3635 3640 3645 3650 3655 3660 3665 3670 3675 3680 3685 3690 3695 3700 3705 3710 3715 3720 3725 3730 3735 3740 3745 3750 3755 3760 3765 3770 3775 3780 3785 3790 3795 3800 3805 3810 3815 3820 3825 3830 3835 3840 3845 3850 3855 3860 3865 3870 3875 3880 3885 3890 3895 3900 3905 3910 3915 3920 3925 3930 3935 3940 3945 3950 3955 3960 3965 3970 3975 3980 3985 3990 3995 4000 4005 4010 4015 4020 4025 4030 4035 4040 4045 4050 4055 4060 4065 4070 4075 4080 4085 4090 4095 4100 4105 4110 4115 4120 4125 4130 4135 4140 4145 4150 4155 4160 4165 4170 4175 4180 4185 4190 4195 4200 4205 4210 4215 4220 4225 4230 4235 4240 4245 4250 4255 4260 4265 4270 4275 4280 4285 4290 4295 4300 4305 4310 4315 4320 4325 4330 4335 4340 4345 4350 4355 4360 4365 4370 4375 4380 4385 4390 4395 4400 4405 4410 4415 4420 4425 4430 4435 4440 4445 4450 4455 4460 4465 4470 4475 4480 4485 4490 4495 4500 4505 4510 4515 4520 4525 4530 4535 4540 4545 4550 4555 4560 4565 4570 4575 4580 4585 4590 4595 4600 4605 4610 4615 4620 4625 4630 4635 4640 4645 4650 4655 4660 4665 4670 4675 4680 4685 4690 4695 4700 4705 4710 4715 4720 4725 4730 4735 4740 4745 4750 4755 4760 4765 4770 4775 4780 4785 4790 4795 4800 4805 4810 4815 4820 4825 4830 4835 4840 4845 4850 4855 4860 4865 4870 4875 4880 4885 4890 4895 4900 4905 4910 4915 4920 4925 4930 4935 4940 4945 4950 4955 4960 4965 4970 4975 4980 4985 4990 4995 5000 5005 5010 5015 5020 5025 5030 5035 5040 5045 5050 5055 5060 5065 5070 5075 5080 5085 5090 5095 5100 5105 5110 5115 5120 5125 5130 5135 5140 5145 5150 5155 5160 5165 5170 5175 5180 5185 5190 5195 5200 5205 5210 5215 5220 5225 5230 5235 5240 5245 5250 5255 5260 5265 5270 5275 5280 5285 5290 5295 5300 5305 5310 5315 5320 5325 5330 5335 5340 5345 5350 5355 5360 5365 5370 5375 5380 5385 5390 5395 5400 5405 5410 5415 5420 5425 5430 5435 5440 5445 5450 5455 5460 5465 5470 5475 5480 5485 5490 5495 5500 5505 5510 5515 5520 5525 5530 5535 5540 5545 5550 5555 5560 5565 5570 5575 5580 5585 5590 5595 5600 5605 5610 5615 5620 5625 5630 5635 5640 5645 5650 5655 5660 5665 5670 5675 5680 5685 5690 5695 5700 5705 5710 5715 5720 5725 5730 5735 5740 5745 5750 5755 5760 5765 5770 5775 5780 5785 5790 5795 5800 5805 5810 5815 5820 5825 5830 5835 5840 5845 5850 5855 5860 5865 5870 5875 5880 5885 5890 5895 5900 5905 5910 5915 5920 5925 5930 5935 5940 5945 5950 5955 5960 5965 5970 5975 5980 5985 5990 5995 6000 6005 6010 6015 6020 6025 6030 6035 6040 6045 6050 6055 6060 6065 6070 6075 6080 6085 6090 6095 6100 6105 6110 6115 6120 6125 6130 6135 6140 6145 6150 6155 6160 6165 6170 6175 6180 6185 6190 6195 6200 6205 6210 6215 6220 6225 6230 6235 6240 6245 6250 6255 6260 6265 6270 6275 6280 6285 6290 6295 6300 6305 6310 6315 6320 6325 6330 6335 6340 6345 6350 6355 6360 6365 6370 6375 6380 6385 6390 6395 6400 6405 6410 6415 6420 6425 6430 6435 6440 6445 6450 6455 6460 6465 6470 6475 6480 6485 6490 6495 6500 6505 6510 6515 6520 6525 6530 6535 6540 6545 6550 6555 6560 6565 6570 6575 6580 6585 6590 6595 6600 6605 6610 6615 6620 6625 6630 6635 6640 6645 6650 6655 6660 6665 6670 6675 6680 6685 6690 6695 6700 6705 6710 6715 6720 6725 6730 6735 6740 6745 6750 6755 6760 6765 6770 6775 6780 6785 6790 6795 6800 6805 6810 6815 6820 6825 6830 6835 6840 6845 6850 6855 6860 6865 6870 6875 6880 6885 6890 6895 6900 6905 6910 6915 6920 6925 6930 6935 6940 6945 6950 6955 6960 6965 6970 6975 6980 6985 6990 6995 7000 7005 7010 7015 7020 7025 7030 7035 7040 7045 7050 7055 7060 7065 7070 7075 7080 7085 7090 7095 7100 7105 7110 7115 7120 7125 7130 7135 7140 7145 7150 7155 7160 7165 7170 7175 7180 7185 7190 7195 7200 7205 7210 7215 7220 7225 7230 7235 7240 7245 7250 7255 7260 7265 7270 7275 7280 7285 7290 7295 7300 7305 7310 7315 7320 7325 7330 7335 7340 7345 7350 7355 7360 7365 7370 7375 7380 7385 7390 7395 7400 7405 7410 7415 7420 7425 7430 7435 7440 7445 7450 7455 7460 7465 7470 7475 7480 7485 7490 7495 7500 7505 7510 7515 7520 7525 7530 7535 7540 7545 7550 7555 7560 7565 7570 7575 7580 7585 7590 7595 7600 7605 7610 7615 7620 7625 7630 7635 7640 7645 7650 7655 7660 7665 7670 7675 7680 7685 7690 7695 7700 7705 7710 7715 7720 7725 7730 7735 7740 7745 7750 7755 7760 7765 7770 7775 7780 7785 7790 7795 7800 7805 7810 7815 7820 7825 7830 7835 7840 7845 7850 7855 7860 7865 7870 7875 7880 7885 7890 7895 7900 7905 7910 7915 7920 7925 7930 7935 7940 7945 7950 7955 7960 7965 7970 7975 7980 7985 7990 7995 8000 8005 8010 8015 8020 8025 8030 8035 8040 8045 8050 8055 8060 8065 8070 8075 8080 8085 8090 8095 8100 8105 8110 8115 8120 8125 8130 8135 8140 8145 8150 8155 8160 8165 8170 8175 8180 8185 8190 8195 8200 8205 8210 8215 8220 8225 8230 8235 8240 8245 8250 8255 8260 8265 8270 8275 8280 8285 8290 8295 8300 8305 8310 8315 8320 8325 8330 8335 8340 8345 8350 8355 8360 8365 8370 8375 8380 8385 8390 8395 8400 8405 8410 8415 8420 8425 8430 8435 8440 8445 8450 8455 8460 8465 8470 8475 8480 8485 8490 8495 8500 8505 8510 8515 8520 8525 8530 8535 8540 8545 8550 8555 8560 8565 8570 8575 8580 8585 8590 8595 8600 8605 8610 8615 8620 8625 8630 8635 8640 8645 8650 8655 8660 8665 8670 8675 8680 8685 8690 8695 8700 8705 8710 8715 8720 8725 8730 8735 8740 8745 8750 8755 8760 8765 8770 8775 8780 8785 8790 8795 8800 8805 8810 8815 8820 8825 8830 8835 8840 8845 8850 8855 8860 8865 8870 8875 8880 8885 8890 8895 8900 8905 8910 8915 8920 8925 8930 8935 8940 8945 8950 8955 8960 8965 8970 8975 8980 8985 8990 8995 9000 9005 9010 9015 9020 9025 9030 9035 9040 9045 9050 9055 9060 9065 9070 9075 9080 9085 9090 9095 9100 9105 9110 9115 9120 9125 9130 9135 9140 9145 9150 9155 9160 9165 9170 9175 9180 9185 9190 9195 9200 9205 9210 9215 9220 9225 9230 9235 9240 9245 9250 9255 9260 9265 9270 9275 9280 9285 9290 9295 9300 9305 9310 9315 9320 9325 9330 9335 9340 9345 9350 9355 9360 9365 9370 9375 9380 9385 9390 9395 9400 9405 9410 9415 9420 9425 9430 9435 9440 9445 9450 9455 9460 9465 9470 9475 9480 9485 9490 9495 9500 9505 9510 9515 9520 9525 9530 9535 9540 9545 9550 9555 9560 9565 9570 9575 9580 9585 9590 9595 9600 9605 9610 9615 9620 9625 9630 9635 9640 9645 9650 9655 9660 9665 9670 9675 9680 9685 9690 9695 9700 9705 9710 9715 9720 9725 9730 9735 9740 9745 9750 9755 9760 9765 9770 9775 9780 9785 9790 9795 9800 9805 9810 9815 9820 9825 9830 9835 9840 9845 9850 9855 9860 9865 9870 9875 9880 9885 9890 9895 9900 9905 9910 9915 9920 9925 9930 9935 9940 9945 9950 9955 9960 9965 9970 9975 9980 9985 9990 9995 9999

Examples 20-21

Example 20, was as Example 19 except that the potassium hydroxide was replaced by 10.7g rubidium hydroxide.

The product after 7 days at 180°C was rubidium, sodium TEPA Nu-10 of $\text{SiO}_2/\text{Al}_2\text{O}_3 = 500$.

Example 21 was as Example 19 except that the potassium hydroxide was replaced by 18.7g caesium hydroxide.

The product after 5 days at 200°C was caesium, sodium Nu-10 plus about 10% each of α -cristobalite and zeolite ZSM-48.

Example 22

This Example was the same as Example 19 except that 1g of boric acid was added to the potassium hydroxide, sodium aluminate solution. The product after 8 days at 160°C was Nu-10 of $\text{SiO}_2/\text{Al}_2\text{O}_3 = 475$ and $\text{SiO}_2/\text{B}_2\text{O}_3 = 640$. About 10% α -cristobalite was present as an impurity.

Example 23

This Example was as Example 19 except that 1.5g antimonious oxide was stirred into the final reaction mixture. The product after 8 days at 160°C contained 0.3% w/w Sb_2O_3 .

Examples 24 - 25

In these Examples, other additives were mixed into Example 19 type reactions and reaction was for 8 days at 160°C. The additives were dissolved in the water prior to dispersing the solid silica.

In Example 24, the addition was 2g potassium chrome alum and the dried Nu-10 product had a $\text{SiO}_2/\text{Al}_2\text{O}_3 = 600$ and a $\text{SiO}_2/\text{Cr}_2\text{O}_3 = 1100$

In Example 25, the additive was 0.7g disodium hydrogen phosphate and the Nu-10 product had a $\text{SiO}_2/\text{Al}_2\text{O}_3 = 700$ and a $\text{SiO}_2/\text{P} = 830$.

Example 26

The synthesis mixture had the following molar composition

4.2 K₂O, 17 TEPA, 50 SiO₂, 2500 H₂O.

46.2g Aerosil 200 were dispersed in a mixture of 49.4g

5 TEPA and 643g water. Next, 2.4g Kaiser S.A. alumina

(Al₂O₃, 3H₂O) was dissolved in a solution of 7.2g

potassium hydroxide in 24g water. The aluminate was

stirred into the silica dispersion and the mixture was

reacted for 8 days at 180°C. The product was potassium

10 Nu-10 having SiO₂/Al₂O₃ = 47.

Example 27

This example illustrates the use of HNu-10 as a catalyst

for toluene methylation. Zeolite HNu-10 was prepared as

described in Example 8.

15 Approximately 2g of this batch of HNu-10 was com-
pressed, crushed and sieved. 0.35 g of 250-500 μ HNu-10
catalyst particles were loaded into a microreactor in which
the zeolite was tested for toluene methylation with methanol
as methylating agent. Prior to contact with reactants,

20 the catalyst bed was flushed with nitrogen at 450°C for
about 1 hour. A feed consisting of toluene and methanol
in a 3:1 molar ratio of the aromatic compound to the
alcohol was vaporised and passed over the catalyst at
450°C at a WHSV of about 7.7. The progress of the reaction

25 is outlined by the results in Table 13.

The proportion of p-xylene in the xylenes fraction
is clearly considerably in excess of the equilibrium con-
centration of 24% and the selectivity to xylenes in the
methylated products is also high. The trimethylbenzenes
30 produced in this test were predominantly 1,2,4-trimethyl-
benzene (~90%). This test, with a calcination of the
catalyst included, demonstrates that the catalyst can be
regenerated to give approximately the same level of
activity and selectivity in the conversion of toluene to
35 methylated products and, in particular, p-xylene.

TABLE 19

| Time on Stream hrs | Conversion of Toluene to methylated product wt % | Mol % of Methylated Product Xylenes | Wt % p-xylene in xylenes fraction |
|--------------------|--|-------------------------------------|--|
| 1.75 | 16.1 | 91.2 | 8.8 |
| 13.00 | 6.5 | 94.6 | 5.4 |
| 25.00 | | | 62.7 |
| | | | Reactant flow ceased; after N ₂ flush, the catalyst was calcined in the reactor at 530°C for 16 hours with about 60 ml m ⁻¹ flow of air. |
| 1.35* | 17.2 | 90.6 | 9.4 |
| | | | 64.0 |

*after recommencement of reactant mixture flow, reactor temp. 450°C

Example 28

This Example illustrates the use of HNu-10 as a catalyst for toluene methylation. Zeolite HNu-10 was prepared as described in Example 9.

5 Approximately 2g of this batch of HNu-10 was compressed, crushed and sieved. 0.37 g of 250-500 μ HNu-10 catalyst particles were loaded into a microreactor and tested in a similar fashion to that described in Example 16 except that the WHSV was about 7.4. The progress of 10 the reaction is outlined by the results in Table 14.

10 It is clear that the proportion of p-xylene in the xylenes fraction is considerably in excess of the equilibrium concentration of 24% and the selectivity to xylenes in the methylated products is also high. The 15 trimethylbenzenes produced in the test were predominantly 1,2,4-trimethylbenzene (~ 90%).

The results of this test are thought to be characteristic of a relatively pure specimen of HNu-10.

Example 29

20 This Example illustrates the use of HNu-10 as a catalyst for toluene methylation. The HNu-10 used in this test was prepared using triethylenetetramine as described in Example 12.

25 Approximately 2g of this HNu-10 was compressed, crushed and sieved. 0.34 g of 250-500 μ catalyst particles were loaded into a microreactor and heated to 450°C in a stream of nitrogen. A feedstock consisting of toluene and methanol in a 3:1 molar ratio was reacted with the catalyst in the microreactor in a similar way to 30 that described in Example 16, except that the flow rate was equivalent to a WHSV of about 9.25. The progress of this test, carried out at approximately atmospheric pressure, is outlined by the results in Table 15.

35 It is clear that the proportion of p-xylene in the xylenes fraction is considerably in excess of the

TABLE 14.

| Time on Stream hrs | Conversion of Toluene to methylated product wt % | Mol % of Methylated Product Xylenes | Wt % p-xylene in xylenes fraction Trimethylbenzenes |
|--------------------|--|-------------------------------------|---|
| 3.85 | 28.2 | 87.1 | 12.9 |
| 4.85 | 25.1 | 88.2 | 11.8 |
| 5.75 | | | 62.8 |
| 3.50* | 23.4 | 89.9 | 10.1 |
| | | | 61.7 |

Reactant mixture flow stopped; the catalyst was purged for 16 hours with nitrogen at 450°C.

* After recommencement of reactant mixture flow to catalyst.

TABLE 15

| Time on stream hrs | Toluene Conversion wt % | Mol % methylated products | | Mol % p-xylene in xylenes fraction |
|-----------------------|----------------------------|---------------------------|-------------------|---------------------------------------|
| | | Xylenes | Trimethylbenzenes | |
| 3.3 | 19.4 | 92.0 | 8.0 | 58.9 |
| 6.1 | 16.2 | 92.1 | 7.9 | 57.6 |

equilibrium concentration of 24% and the selectivity to xylenes in the methylated products is also high.

Example 30

5 This Example is used to illustrate the effectiveness of HNu-10 as a catalyst for toluene disproportionation. The HNu-10 used in this test was that prepared in Example 8.

10 Approximately 2g of this HNu-10 was compressed, crushed and sieved. 0.38 g of 250-500 μ HNu-10 catalyst particles were loaded into a microreactor and heated to 530°C in a stream of nitrogen. The sample was maintained at this temperature in a stream of nitrogen for a further hour before toluene was passed to the catalyst. Toluene was vaporised and fed to the catalyst at a rate equivalent to a WHSV of 11.1. The progress of this test, carried out at approximately atmospheric pressure and with neat toluene feed, is outlined by the results given in Table 16.

TABLE 16

| Time on stream hrs | Toluene Conversion wt % | Mol % p-xylene in Xylenes fraction |
|--------------------|-------------------------|------------------------------------|
| 1.0 | 5.4 | 31.9 |
| 3.1 | 0.7 | 51.2 |

30 It will be evident that the amount of p-xylene present in the xylenes fraction is greater than that found in an equilibrium mixture (~ 24% p-xylene) but the catalyst shows relatively low activity for toluene disproportionation.

Example 31

A sample of sodium TEPA Nu-10 prepared as described in Example 8 was calcined at 550°C for 16 hours in air. The calcined material was then slurry-exchanged with 50 ml N/1 NH₄Cl per g of zeolite for 16 hours at 100°C. The sample was filtered, washed with distilled water and then dried at 110°C. The NH₄-NU-10 was then calcined at 550°C for 16 hours in air to produce H-Nu-10. Chemical analysis of the resulting material indicated that 10 it had the following molar composition ignoring hydrogen:



In a continuous flow reactor, about 1 g of the catalyst, particle size 710-1000 μ , was tested for methanol conversion. The catalyst was activated at 450°C under helium for 1 hour. The temperature was reduced to 400°C then methanol in helium was passed over the catalyst. The conditions and analysis of the C₁-C₄ hydrocarbons obtained can be seen in Table 17, Example 31A. After several hours, the catalyst was removed from the reactor, regenerated under air at 550°C for 16 hours then re-tested for methanol conversion. The conditions used and distribution of the C₁-C₄ hydrocarbons obtained can be seen in Table 17, Example 31B.

TABLE 17

| | | Ex 31A | Ex 31B |
|----|---|--------|--------|
| 25 | Temp/°C | 400 | 400 |
| | Conc of Methanol in Helium | 20% | 18% |
| | WHSV Methanol | 1 | 1 |
| | Conversion | 100% | 100% |
| 30 | Distribution % (w/w) C ₁ -C ₄ Hydrocarbons Obtained | | |
| | Methane | 2.9 | 1.7 |
| | Ethane | | - |
| | Ethylene | 6.9 | 7.4 |
| | Propane | 6.0 | 6.4 |
| 35 | Propylene | 44.6 | 42.7 |
| | Butanes | 3.0 | 3.3 |
| | Butylenes | 36.7 | 38.5 |

Example 32

5 A sample of sodium TEPA Nu-10 prepared as described below was calcined and ion-exchanged by a procedure similar to that described in Example 1. Chemical analysis of the resulting material indicated that it had the following molar composition ignoring hydrogen:



10 In a continuous flow reactor, about 1 g of the catalyst, particle size 710-1000 μ , was tested for methanol conversion. The catalyst was activated at 450°C under helium for 1 hour then methanol in helium was passed over the catalyst. The reaction conditions and analysis of the C₁-C₄ hydrocarbons obtained can be seen in Table 18, Example 32A. After examination, the catalyst was removed from the reactor, regenerated under air at 15 550°C for 16 hours then re-tested for methanol conversion. After activation at 450°C for 1 hour under helium, the temperature was decreased to 350°C then 55% methanol in helium was passed over the catalyst. Reaction details 20 and analysis of the C₁-C₄ hydrocarbons produced can be seen in Table 18, Example 32B.

TABLE 18

| | | <u>Ex 32A</u> | <u>Ex 32B</u> |
|--|-----------|---------------|---------------|
| 25 | Temp/°C | 450 | 350 |
| Conc of Methanol in Helium | | 65% | 55% |
| WHSV Methanol | | 1 | 1 |
| Conversion | | 100% | >90% |
| Distribution % (w/w) C ₁ -C ₄ hydrocarbons obtained. | | | |
| 30 | Methane | 13.4 | 9.5 |
| Ethane | | 1.7 | 1.4 |
| Ethylene | | 11.3 | 3.5 |
| Propane | | 13.0 | 20.3 |
| Propylene | | 34.6 | 28.9 |
| Butanes | | 1.3 | 6.1 |
| 35 | Butylenes | 24.8 | 30.4 |

For the preparation of the zeolite Nu-10, the reaction mixture had the following composition :

2.3 Na₂O, 27.5 TEPA, 94SiO₂, 3800H₂O, 53 NaCl
 58 g tetraethylenepentamine were dispersed in 215 g Syton X-30 of molar composition 31.65Na₂O, Al₂O₃, 2409SiO₂, 21076H₂O, followed by a solution of 2.1 g sodium aluminate (1.22 Na₂O, Al₂O₃, 1.2H₂O) in 10 g water. Finally, a solution of 34.5 g sodium chloride in 598 g water was stirred in. Stirring continued for 30 minutes to homogenize the mixture. The reaction was carried out in a 1 litre stirred stainless steel autoclave for 114 hours at 150°C. After filtration, washing and drying, the product was sodium TEPA - Nu-10 with no detectable impurities other than a slight trace of sodium chloride.

Example 33

A sample of Nu-10 prepared and activated as in Example 32 was further tested for aromatics production from methanol. A mixture of methanol in nitrogen (65% methanol) was passed over the catalyst at 450°C. The reaction conditions and hydrocarbon analysis are given in Table 19.

TABLE 19

| | |
|--------------------------------------|---|
| Temperature/°C | 450 |
| Conc of methanol % in nitrogen | 65 |
| WHSV Methanol | 1 |
| Methanol conversion % | 100 |
| The hydrocarbons produced comprised: | C ₁ -C ₅ aliphatics 92 wt % Aromatics 7 wt % Higher aliphatics traces |
| Analysis of the aromatics showed: | Benzene 1.5% Toluene 16% Ethylbenzene 3.5% Xylenes 40% C ₉ aromatics 39% |

Example 34

The reaction mixture had the following molar composition:

5.9 K_2O , 10 TEPA, Al_2O_3 , 30 SiO_2 , 1500 H_2O
5 45g Aerosil 200 were dispersed in a mixture of 47.3g TEPA and 650g water. Next, 3.9g alumina were dissolved in 16.6 KOH and 27g water. The aluminate solution was stirred into the slurry and the mixture was reacted for 64 hours at 180°C. The product was potassium TEPA
10 Nu-10 containing traces a cristobalite and a ZSM5 type zeolite. The SiO_2/Al_2O_3 ratio of this product was 25.

CLAIMS

1. A synthetic zeolite material having a molar composition expressed by the formula:

0.5 to 1.5 $R_2O : Y_2O_3 : \text{at least } 20 XO_2 : 0 \text{ to } 4000 H_2O$
 wherein R is a monovalent cation or 1/n of a cation of valency n, X is silicon and/or germanium, Y is one or more of aluminium, iron, chromium, vanadium, molybdenum, arsenic, antimony, manganese, gallium or boron, and H_2O is water of hydration additional to water notionally present when R is H, and having an X-ray pattern substantially as set out in Table 1...

2. A synthetic zeolite material according to claim 1 having a molar composition expressed by the formula:

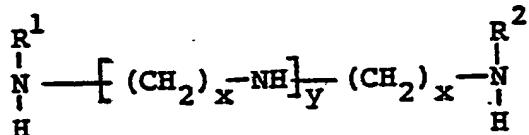
0.5 to 1.5 $H_2O : Y_2O_3 : \text{at least } 60 XO_2 : 0 \text{ to } 200 H_2O$

3. A synthetic zeolite material according to claim 1 having a molar composition expressed by the formula:

0.5 to 1.5 $H_2O : Y_2O_3 : 20 \text{ to } 5000 XO_2 : 0 \text{ to } 4000 H_2O$

4. A synthetic zeolite material according to any one of claims 1 to 3 wherein R is or includes hydrogen.

5. A method of making a synthetic zeolite material as defined in claim 1 which comprises reacting an aqueous mixture containing at least one oxide XO_2 , at least one oxide Y_2O_3 and at least one polyalkylene polyamine having the formula



wherein each of R^1 and R^2 , independently, represent hydrogen or a C_1-C_6 alkyl group, x is an integer from 2 to 6 and y is an integer from 0 to 10, provided that when y is 0, x is from 2 to 5.

6. A method according to claim 5 wherein the aqueous mixture has the molar composition:

| | |
|---------------|------------------|
| XO_2/Y_2O_3 | 25 to 5000 |
| M^1OH/XO_2 | 10^{-8} to 1.0 |
| H_2O/XO_2 | 10 to 200 |
| Q/XO_2 | 0.05 to 4 |
| M^2Z/XO_2 | 0 to 4 |

wherein X and Y have the meanings given in claim 1, each of M^1 and M^2 , independently, is an alkali metal, ammonium or hydrogen, Q is the polyalkylene polyamine and Z is a strong acid radical.

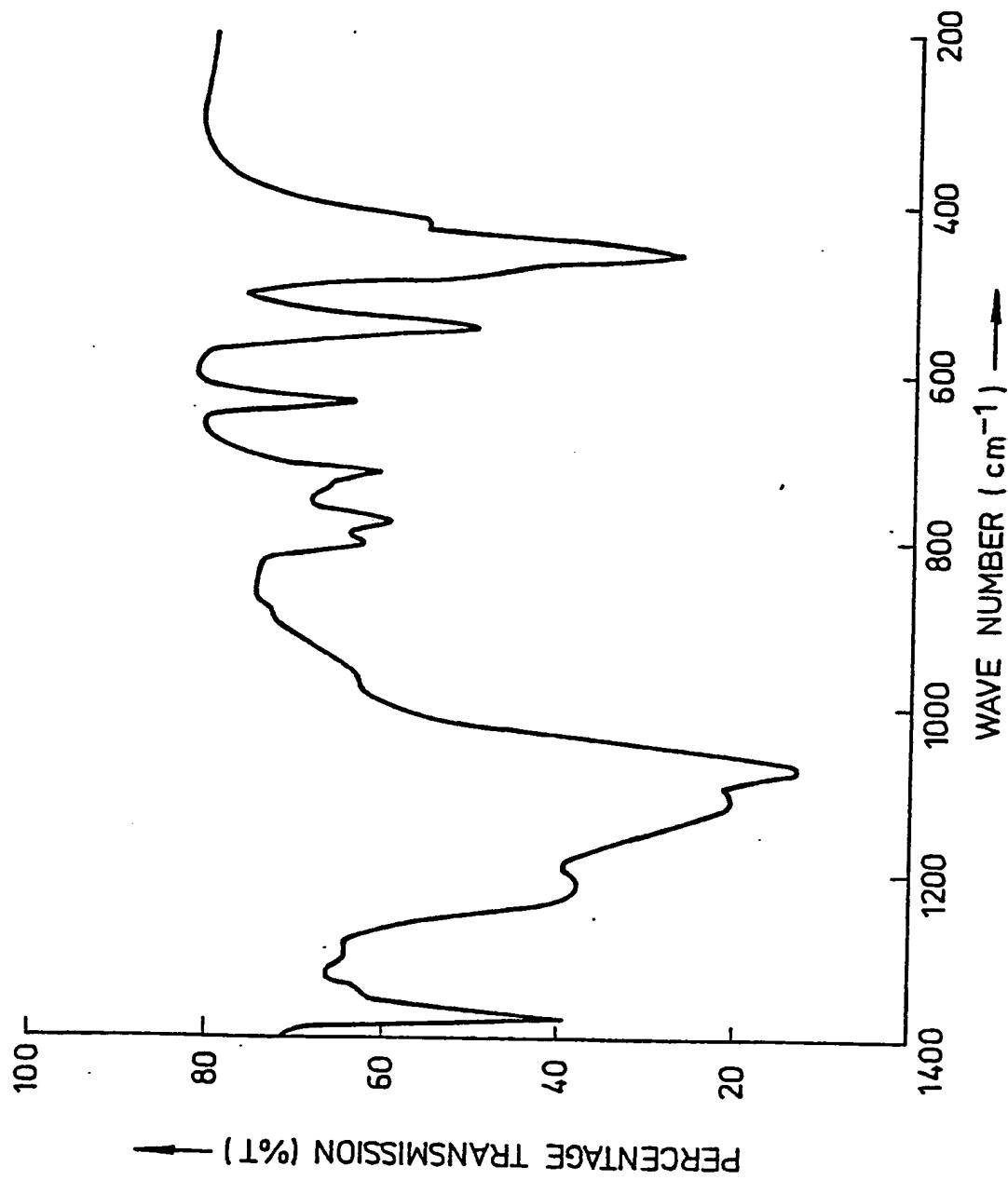
7. A method according to claim 6 wherein XO_2/Y_2O_3 is in the range 40 to 1000.
8. A method according to claim 7 wherein XO_2/Y_2O_3 is in the range 80 to 500.
9. A method according to any one of claims 5 to 8 wherein the polyalkylene polyamine is triethylene tetramine or tetraethylene pentamine.
10. A catalyst comprising a synthetic zeolite material as claimed in any one of claims 1 to 4.
11. A catalytic process employing the catalyst claimed in claim 10.
12. A process according to claim 11 wherein an alkylbenzene or a mixture of alkylbenzenes is reacted with an alkylating agent under alkylation conditions.
13. A process according to claim 12 wherein toluene is reacted with methanol to form a mixture of xylene isomers.
14. A process according to claim 11 wherein a lower monohydric alcohol or an ether derived therefrom is converted to hydrocarbons.
15. A process according to claim 14 wherein methanol or dimethyl ether is converted to lower olefins.

K STEPHENSON

AGENTS FOR THE APPLICANT

11

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